

Polysiloxanes Containing Alkyl Side Groups: Synthesis and Mesomorphic Behavior

Byoung Gak Kim, Jin-Kyung Moon, Eun-Ho Sohn, and Jong-Chan Lee*

Department of Chemical and Biological Engineering, College of Engineering, Seoul National University, Seoul 151-744, Korea

Jong-Kee Yeo

LG Chem. Ltd., 20 Yeouido-dong, Yeongdeungpo-gu, Seoul 150-721, Korea

Received July 21, 2007; Revised September 17, 2007

Abstract: A series of polysiloxanes containing alkylsulfonyl side groups were synthesized using a polymer analogous reaction beginning from poly(methylhydrosiloxane) and the corresponding olefins. These polymers showed a mesomorphic behavior with smectic liquid crystalline phases. The chemical and physical properties of these polymers were examined using nuclear magnetic resonance spectroscopy, gel permeation chromatography, differential scanning calorimetry, optical polarizing microscopy, and X-ray diffraction.

Keywords: polysiloxane, hydrosilylation, liquid crystal, thioether, sulfone, alkyl side group.

Introduction

Thermotropic liquid crystalline polymers have been the subject of much interest for both fundamental and applied research.¹ The rod-like mesogenic groups composed of two or more cyclic rings are the basic unit for formation of liquid crystalline polymers.² Main chain and side chain liquid crystalline polymers can be prepared by incorporating these mesogenic groups into the backbone and side groups, respectively, in the polymer.³ Interestingly silicon polymers containing two *n*-alkyl groups, where the *n*-alkyl group is longer than a methyl group, show thermotropic liquid crystalline phases although these polymers do not have the mesogenic groups.^{4,5} This unusual liquid crystalline behavior of these polymers results from the biphilicity that occurs between interaction of the inorganic silicone backbone and organic alkyl side groups, as well as the full symmetry of the polymers. The biphilicity and the symmetry can induce the rigid polymer structure, which in turn produces the mesogenic property. In contrast, poly(methylalkylsiloxane)s with only one longer alkyl group do not have liquid crystallinity, possibly because the polymer structure is not symmetric or these structure cannot produce phase separation to induce biphilicity.⁶ Aliphatic polysulfones are another unique class of polymers that show liquid crystalline behavior without mesogenic groups.⁷ The liquid crystallinity of these polymers results from the strong dipole-dipole interactions between the sulfone groups, which create the stiff section or the mesogenic unit in the polymer.⁸

We synthesized a series of poly(alkylsulfonylpropylmeth-

ylsiloxane)s with different alkyl groups. Since there is only one longer alkyl group in the siloxane backbone of the polymer, we did not expect the biphilicity or symmetric structure formation that generates the mesogenic phase. However the alkylsulfone groups in the polymer might create a mesogenic unit to generate the liquid crystalline phases. Here, we found that these polymers show thermotropic liquid crystalline phases. The detailed synthetic procedures and characterization of these polymers are discussed in this paper.

Experimental

Materials. Poly(methylhydrosiloxane) (PMHS) (Gelest Inc.) was used as received. M_n and M_w of PMHS were 2,200 and 3,300, respectively. Toluene and tetrahydrofuran were distilled from benzophenone and sodium metal and stored under dry nitrogen. Absolute ethanol was dried over molecular sieves (4 Å). All other reagents and solvents were used as received. Hydrogen hexachloroplatinate (IV) hydrate and *n*-alkanethiols were commercially available and received from Aldrich. Sodium *n*-alkanethiolates were prepared by adding *n*-alkanethiols (30 mmol) to a solution of sodium ethoxide (33 mmol) in ethanol (66 mL); the solid residuals obtained after evaporation of the solvent was washed with ether, filtered, and dried under vacuum.

Characterization. ¹H and ¹³C-NMR spectra were measured in CDCl₃ at 300 MHz (Bruker, Avance DPX-300). 2-Dimensional heterogeneous NMR spectra were obtained using 600 MHz (Bruker, Avance 600). IR spectra were obtained using a Bomem MB 100 Fourier transform infrared spectrophotometer in combination with a deuterated triglycine sulfate

*Corresponding Author. E-mail: jongchan@snu.ac.kr

(DTGS) detector. The polymer samples were cast onto a potassium bromide (KBr) window. Differential scanning calorimetry (DSC) was carried out on a TA instruments 2920 differential scanning calorimeter. The heating and cooling rates were 10 °C/min. Molar mass and polydispersity index were obtained using a Viscotek Model 250 gel permeation chromatograph (GPC) with differential refractometer as a detector. All polarizing optical microscopy images were recorded with Leica DM-LP polarizing optical microscope equipped with a Mettler FP82HT hot-stage controlled by Mettler FP90 central processor. Small-angle X-ray scattering (SAXS) measurements were performed using a Bruker-AXS Nanostar instrument with a sealed tube CuK_α X-ray source ($\lambda=1.5418 \text{ \AA}$) operated at 30 mA and 45 kV and a 2D Histar detector. The direction of the X-ray beam was perpendicular to the vector of the applied electric field. The scattering patterns were corrected for the beam stop and background prior to further evaluations. X-ray diffraction patterns were performed by a wide angle X-ray scattering (WAXS) with general area detector diffraction (GADDS) (Bruker, Germany) using Ni-filtered CuK_α radiation (35 kV, 15 mA). Synchrotron X-ray scattering experiments were conducted using the beam line (3C2) at the Pohang Light Source, Korea. The temperature was controlled with the accuracy of $\pm 1 \text{ }^\circ\text{C}$ in the experimental temperature range.

Synthesis.

Preparation of (3-*n*-alkylthio)propenes: The following procedure was used to synthesize (3-*n*-alkylthio)propene. The synthesis is exemplified in the case of (3-*n*-octylthio)propene. To a stirred solution of sodium *n*-octylthiolate (30 mmol) in THF was added allyl bromide (42 mmol). After stirring for 6 h at 40 °C, the mixture was extracted with methylene chloride (150 mL) and washed with distilled water three times. The organic layer was dried over magnesium sulfate, filtered, and evaporated under reduced pressure. The crude product was purified with column chromatography packed with silica gel in *n*-hexane. (3-*n*-Decylthio)propene, (3-*n*-dodecylthio)propene, (3-*n*-tetradecylthio)propene, and (3-*n*-hexadecylthio)propene were synthesized using the same procedure used for the synthesis of (3-*n*-octylthio)propene, except that sodium *n*-decylthiolate, sodium *n*-dodecylthiolate, sodium *n*-tetradecylthiolate, sodium *n*-hexadecylthiolate, respectively, were used instead of sodium *n*-octylthiolate. The yields were always above 70%.

(3-*n*-Octylthio)propene $^1\text{H-NMR}$ (CDCl_3 , TMS, ppm): $\delta = 0.85\text{--}0.89$ (t, 3 H), 1.25 (s, 12 H), 2.41-2.46 (t, 2 H), 3.09-3.15 (d, 2 H), 5.04-5.10 (m, 2 H), 5.70-5.85 (m, 1 H).

(3-*n*-Decylthio)propene $^1\text{H-NMR}$ (CDCl_3 , TMS, ppm): $\delta = 0.85\text{--}0.89$ (t, 3 H), 1.25 (s, 16 H), 2.41-2.46 (t, 2 H), 3.09-3.16 (d, 2 H), 5.04-5.10 (m, 2 H), 5.71-5.85 (m, 1 H).

(3-*n*-Dodecylthio)propene $^1\text{H-NMR}$ (CDCl_3 , TMS, ppm): $\delta = 0.84\text{--}0.89$ (t, 3 H), 1.24 (s, 20 H), 2.40-2.45 (t, 2 H), 3.09-3.11 (d, 2 H), 5.03-5.09 (m, 2 H), 5.70-5.84 (m, 1 H).

(3-*n*-Tetradecylthio)propene $^1\text{H-NMR}$ (CDCl_3 , TMS, ppm):

$\delta = 0.85\text{--}0.89$ (t, 3 H), 1.24 (s, 24 H), 2.41-2.46 (t, 2 H), 3.09-3.15 (d, 2 H), 5.04-5.10 (m, 2 H), 5.70-5.85 (m, 1 H).

(3-*n*-Hexadecylthio)propene $^1\text{H-NMR}$ (CDCl_3 , TMS, ppm): $\delta = 0.85\text{--}0.89$ (t, 3 H), 1.25 (s, 28 H), 2.40-2.46 (t, 2 H), 3.09-3.15 (d, 2 H), 5.04-5.10 (m, 2 H), 5.70-5.84 (m, 1 H).

Preparation of (3-*n*-alkylthio)propyl-substituted Poly(methylsiloxane)s (nTPs): The acronym of (3-*n*-alkylthio)propyl-substituted poly(methylsiloxane) is nTP where *n* is the number of carbon in the alkylthio side group. The following procedure was used to synthesize (3-*n*-alkylthio)propyl-substituted poly(methylsiloxane) (8TP). The synthesis is exemplified in the case of 8TP. The (3-*n*-octylthio)propene (24 mmol, 10 mol% excess versus the Si-H groups in PMHS) was dissolved in 150 mL of freshly distilled toluene containing an appropriate amount of PMHS. The reaction mixture was heated to 70 °C and stirred under nitrogen. At this point, 0.008 g of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was added as a solution in EtOH (20 mg/mL). The resulting solution was stirred at 70 °C for 3 days. After removal of the toluene, the polymers were purified by several washes with methanol. The polymer was dried under high vacuum at room temperature overnight. The yield was 73%. The conversion from PMHS to the product calculated by comparing the area of the triplet at 0.88 ppm from the methyl group at the side chain end and that of the singlet at 4.8 ppm from the backbone was about 95%. (3-*n*-Decylthio)propyl-substituted poly(methylsiloxane) (10TP), (3-*n*-dodecylthio)propyl-substituted poly(methylsiloxane) (12TP), (3-*n*-tetradecylthio)propyl-substituted poly(methylsiloxane) (14TP), and (3-*n*-hexadecylthio)propyl-substituted poly(methylsiloxane) (16TP) were synthesized using the same procedure used for the synthesis of 8TP except that (3-*n*-decylthio)propene, (3-*n*-dodecylthio)propene, (3-*n*-tetradecylthio)propene, and (3-*n*-hexadecylthio)propene, respectively, were used instead of (3-*n*-octylthio)propene. The yields were above 70% and the conversions calculated from $^1\text{H-NMR}$ spectra were always larger than 95%.

8TP $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.11$ (s, 3H, -Si- CH_3), 0.65 (t, 2H, -Si- $\text{CH}_2\text{-CH}_2\text{-}$), 0.88 (t, 3 H, -(CH_2) $_7$ - CH_3), 1.06 (d, 3H, -Si- $\text{CHCH}_3\text{-CH}_2\text{-S-}$), 1.27 (m, 10H, -S- $\text{CH}_2\text{-CH}_2\text{-(CH}_2$) $_5$ - CH_3), 1.29 (m, 2H, -Si- $\text{CHCH}_3\text{-CH}_2\text{-S-}$) 1.57 (m, 2H, -S- $\text{CH}_2\text{-CH}_2\text{-(CH}_2$) $_5$ -), 1.61 (m, 2H, -Si- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-S-}$), 2.30 and 2.82 (m, 2H, -Si- $\text{CHCH}_3\text{-CH}_2\text{-S-}$), 2.48 (t, 2H, -S- $\text{CH}_2\text{-(CH}_2$) $_6$ -), 2.51 (m, 2H, -Si-(CH_2) $_2$ - $\text{CH}_2\text{-S-CH}_2\text{-}$).

$^{13}\text{C-NMR}$ (CDCl_3): $\delta = -0.1$ (s, 1C, -Si- CH_3), 13.26 (s, 1C, -Si- $\text{CHCH}_3\text{-CH}_2\text{-S-}$), 14.38 (s, 1C, -(CH_2) $_7$ - CH_3), 17.45 (s, 1C, -Si- $\text{CH}_2\text{-CH}_2\text{-}$), 21.69 (s, 1C, -Si- $\text{CHCH}_3\text{-CH}_2\text{-S-}$), 22.97 (s, 1C, -(CH_2) $_6$ - $\text{CH}_2\text{-CH}_3$), 23.67 (s, 1C, -Si- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-S-}$), 29.34-32.16 (s, 4C, -S- $\text{CH}_2\text{-CH}_2\text{-(CH}_2$) $_4$ -), 30.03 (s, 1C, -S- $\text{CH}_2\text{-CH}_2\text{-(CH}_2$) $_5$ -), 32.51 and 32.65 (s, 1C, - $\text{CHCH}_3\text{-CH}_2\text{-S-CH}_2\text{-}$ and - $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-S-CH}_2\text{-}$), 35.24 (s, 1C, -Si- $\text{CHCH}_3\text{-CH}_2\text{-S-}$), 35.83 (s, 1C, -Si-(CH_2) $_2$ - $\text{CH}_2\text{-S-}$).

10TP $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.11$ (s, 3H, -Si- CH_3), 0.65 (t, 2H, -Si- $\text{CH}_2\text{-CH}_2\text{-}$), 0.88 (t, 3 H, -(CH_2) $_9$ - CH_3), 1.06 (d, 3H, -Si- $\text{CHCH}_3\text{-CH}_2\text{-S-}$), 1.27 (m, 14H, -S- $\text{CH}_2\text{-CH}_2\text{-(CH}_2$) $_7$ -

CH₃), 1.29 (m, 2H, -Si-CHCH₃-CH₂-S-) 1.57 (m, 2H, -S-CH₂-CH₂-(CH₂)₇-), 1.63 (m, 2H, -Si-CH₂-CH₂-CH₂-S-), 2.28 and 2.83 (m, 2H, -Si-CHCH₃-CH₂-S-), 2.48 (t, 2H, -S-CH₂-(CH₂)₈-), 2.51 (m, 2H, -Si-(CH₂)₂-CH₂-S-CH₂-).

¹³C-NMR (CDCl₃): δ = -0.1 (s, 1C, -Si-CH₃), 13.26 (s, 1C, -Si-CHCH₃-CH₂-S-), 14.29 (s, 1C, -(CH₂)₉-CH₃), 17.40 (s, 1C, -Si-CH₂-CH₂-), 21.74 (s, 1C, -Si-CHCH₃-CH₂-S-), 22.92 (s, 1C, -(CH₂)₆-CH₂-CH₃), 23.70 (s, 1C, -Si-CH₂-CH₂-CH₂-S-), 29.26-32.60 (s, 6C, -S-CH₂-CH₂-(CH₂)₆-), 30.00 (s, 1C, -S-CH₂-CH₂-(CH₂)₇-), 32.51 and 32.65 (s, 1C, -CHCH₃-CH₂-S-CH₂- and -CH₂-CH₂-CH₂-S-CH₂-), 35.24 (s, 1C, -Si-CHCH₃-CH₂-S-), 35.83 (s, 1C, -Si-(CH₂)₂-CH₂-S-).

12TP ¹H-NMR (CDCl₃): δ = 0.11 (s, 3H, -Si-CH₃), 0.65 (t, 2H, -Si-CH₂-CH₂-), 0.88 (t, 3 H, -(CH₂)₁₁-CH₃), 1.06 (d, 3H, -Si-CHCH₃-CH₂-S-), 1.26 (m, 18H, -S-CH₂-CH₂-(CH₂)₉-CH₃), 1.29 (m, 2H, -Si-CHCH₃-CH₂-S-) 1.57 (m, 2H, -S-CH₂-CH₂-(CH₂)₉-), 1.61 (m, 2H, -Si-CH₂-CH₂-CH₂-S-), 2.30 and 2.86 (m, 2H, -Si-CHCH₃-CH₂-S-), 2.48 (t, 2H, -S-CH₂-(CH₂)₁₀-), 2.51 (m, 2H, -Si-(CH₂)₂-CH₂-S-CH₂-).

¹³C-NMR (CDCl₃): δ = -0.1 (s, 1C, -Si-CH₃), 13.54 (s, 1C, -Si-CHCH₃-CH₂-S-), 14.74 (s, 1C, -(CH₂)₉-CH₃), 17.60 (s, 1C, -Si-CH₂-CH₂-), 22.14 (s, 1C, -Si-CHCH₃-CH₂-S-), 23.31 (s, 1C, -(CH₂)₈-CH₂-CH₃), 24.08 (s, 1C, -Si-CH₂-CH₂-CH₂-S-), 29.05-32.55 (s, 8C, -S-CH₂-CH₂-(CH₂)₈-), 30.45 (s, 1C, -S-CH₂-CH₂-(CH₂)₉-), 33.00 and 33.48 (s, 1C, -CHCH₃-CH₂-S-CH₂- and -CH₂-CH₂-CH₂-S-CH₂-), 35.66 (s, 1C, -Si-CHCH₃-CH₂-S-), 36.18 (s, 1C, -Si-(CH₂)₂-CH₂-S-).

14TP ¹H-NMR (CDCl₃): δ = 0.12 (s, 3H, -Si-CH₃), 0.66 (t, 2H, -Si-CH₂-CH₂-), 0.88 (t, 3 H, -(CH₂)₁₃-CH₃), 1.06 (d, 3H, -Si-CHCH₃-CH₂-S-), 1.26 (m, 22H, -S-CH₂-CH₂-(CH₂)₁₁-CH₃), 1.29 (m, 2H, -Si-CHCH₃-CH₂-S-) 1.58 (m, 2H, -S-CH₂-CH₂-(CH₂)₁₁-), 1.61 (m, 2H, -Si-CH₂-CH₂-CH₂-S-), 2.30 and 2.86 (m, 2H, -Si-CHCH₃-CH₂-S-), 2.48 (t, 2H, -S-CH₂-(CH₂)₁₂-), 2.51 (m, 2H, -Si-(CH₂)₂-CH₂-S-CH₂-).

¹³C-NMR (CDCl₃): δ = -0.1 (s, 1C, -Si-CH₃), 12.93 (s, 1C, -Si-CHCH₃-CH₂-S-), 14.10 (s, 1C, -(CH₂)₁₃-CH₃), 16.88 (s, 1C, -Si-CH₂-CH₂-), 21.35 (s, 1C, -Si-CHCH₃-CH₂-S-), 22.67 (s, 1C, -(CH₂)₁₀-CH₂-CH₃), 23.29 (s, 1C, -Si-CH₂-CH₂-CH₂-S-), 29.05-31.91 (s, 10C, -S-CH₂-CH₂-(CH₂)₁₀-), 29.79 (s, 1C, -S-CH₂-CH₂-(CH₂)₁₁-), 32.17 and 32.31 (s, 1C, -CHCH₃-CH₂-S-CH₂- and -CH₂-CH₂-CH₂-S-CH₂-), 34.87 (s, 1C, -Si-CHCH₃-CH₂-S-), 35.53 (s, 1C, -Si-(CH₂)₂-CH₂-S-).

16TP ¹H-NMR (CDCl₃): δ = 0.12 (s, 3H, -Si-CH₃), 0.67 (t, 2H, -Si-CH₂-CH₂-), 0.88 (t, 3 H, -(CH₂)₁₅-CH₃), 1.08 (d, 3H, -Si-CHCH₃-CH₂-S-), 1.27 (m, 26H, -S-CH₂-CH₂-(CH₂)₁₃-CH₃), 1.29 (m, 2H, -Si-CHCH₃-CH₂-S-) 1.58 (m, 2H, -S-CH₂-CH₂-(CH₂)₁₃-), 1.67 (m, 2H, -Si-CH₂-CH₂-CH₂-S-), 2.30 and 2.81 (m, 2H, -Si-CHCH₃-CH₂-S-), 2.49 (t, 2H, -S-CH₂-(CH₂)₁₄-), 2.51 (m, 2H, -Si-(CH₂)₂-CH₂-S-CH₂-).

¹³C-NMR (CDCl₃): δ = -0.1 (s, 1C, -Si-CH₃), 12.95 (s, 1C, -Si-CHCH₃-CH₂-S-), 14.13 (s, 1C, -(CH₂)₁₆-CH₃), 17.03 (s, 1C, -Si-CH₂-CH₂-), 21.74 (s, 1C, -Si-CHCH₃-CH₂-S-), 22.70 (s, 1C, -(CH₂)₁₂-CH₂-CH₃), 23.70 (s, 1C, -Si-CH₂-CH₂-CH₂-S-), 28.54-31.93 (s, 12C, -S-CH₂-CH₂-(CH₂)₁₂-), 29.66 (s, 1C,

-S-CH₂-CH₂-(CH₂)₁₃-), 32.13 and 32.26 (s, 1C, -CHCH₃-CH₂-S-CH₂- and -CH₂-CH₂-CH₂-S-CH₂-), 34.76 (s, 1C, -Si-CHCH₃-CH₂-S-), 35.65 (s, 1C, -Si-(CH₂)₂-CH₂-S-).

Preparation of (3-*n*-Alkylsulfonyl)propyl-substituted Poly(methylsiloxane) (nSPs): The acronym of (3-*n*-alkylsulfonyl)propyl-substituted poly(methylsiloxane) is nSP where *n* is the number of carbon in the alkylthio side group. The following procedure was used to synthesize (3-*n*-alkylthio)propyl-substituted poly(methylsiloxane). The synthesis is exemplified in the case of (3-*n*-octylsulfonyl)propyl-substituted poly(methylsiloxane) (8SP). To a stirred solution of 8TP (23 mmol of side chain) in methylene chloride (250 mL) was added *m*-chloroperoxybenzoic acid (50.6 mmol). After stirring at room temperature for 1 h, the reaction mixture was concentrated and then poured into methanol. The precipitate was further purified by several precipitations from methylene chloride into methanol and then dried under high vacuum at room temperature overnight. The yield was 92%. The conversion calculated from the ¹H-NMR data by comparing the peak integrals of the side chains and the backbone was almost 100%. (3-*n*-Decylthio)propyl-substituted poly(methylsiloxane) (10SP), (3-*n*-dodecylthio)propyl-substituted poly(methylsiloxane) (12SP), (3-*n*-tetradecylthio)propyl-substituted poly(methylsiloxane) (14SP), and (3-*n*-hexadecylthio)propyl-substituted poly(methylsiloxane) (16SP) were synthesized using the same procedure used for the synthesis of 8SP except that 10TP, 12TP, 14TP, and 16TP, respectively, were used instead of 8TP. The yields were above 90% and the conversions calculated from ¹H-NMR spectra were always about 100%.

8SP ¹H-NMR (CDCl₃): δ = 0.17 (s, 3H, -Si-CH₃), 0.72 (t, 2H, -Si-CH₂-CH₂-), 0.88 (t, 3H, -(CH₂)₇-CH₃), 1.25 (d, 3H, -Si-CHCH₃-CH₂-SO₂-), 1.28 (m, 8H, -SO₂-CH₂-CH₂-CH₂-(CH₂)₄-CH₃), 1.44 (m, 2H, -SO₂-CH₂-CH₂-CH₂-CH₂-), 1.71 (m, 1H, -Si-CHCH₃-CH₂-SO₂-), 1.82 (m, 2H, -SO₂-CH₂-CH₂-CH₂-), 1.90 (m, 2H, -Si-CH₂-CH₂-CH₂-SO₂-), 2.82 and 2.92 (m, 1H, 1H, -Si-CHCH₃-CH₂-SO₂-), 2.96 (m, 2H, -Si-(CH₂)₂-CH₂-SO₂-) 3.12(m, 2H, -SO₂-CH₂-(CH₂)₆-CH₃).

¹³C-NMR (CDCl₃): δ = -0.1 (s, 1C, -Si-CH₃), 14.03 (s, 1C, -Si-CHCH₃-CH₂-SO₂-), 14.64 (s, 1C, -(CH₂)₅-CH₃), 15.91 (s, 1C, -Si-CH₂-CH₂-CH₂-), 16.89 (s, 1C, -Si-CH₂-CH₂-) 22.37 (s, 1C, -Si-CHCH₃-CH₂-SO₂-), 22.40 (s, 1C, -SO₂-CH₂-CH₂-CH₂-), 23.13 (s, 1C, -(CH₂)₆-CH₂-CH₃), 29.05-32.31 (s, 4C, -SO₂-CH₂-CH₂-(CH₂)₄-CH₂-CH₃), 53.79 (s, 1C, -Si-CH₂-CH₂-CH₂-SO₂-), 54.65 (s, 1C, -Si-CHCH₃-CH₂-SO₂-), 55.53 (s, 2C, -SO₂-CH₂-CH₂-).

10SP ¹H-NMR (CDCl₃): δ = 0.17 (s, 3H, -Si-CH₃), 0.72 (t, 2H, -Si-CH₂-CH₂-), 0.88 (t, 3H, -(CH₂)₉-CH₃), 1.25 (d, 3H, -Si-CHCH₃-CH₂-SO₂-), 1.26 (m, 12H, -SO₂-CH₂-CH₂-CH₂-(CH₂)₆-CH₃), 1.42 (m, 2H, -SO₂-CH₂-CH₂-CH₂-CH₂-), 1.71 (m, 1H, -Si-CHCH₃-CH₂-SO₂-), 1.81 (m, 2H, -SO₂-CH₂-CH₂-CH₂-), 1.88 (m, 2H, -Si-CH₂-CH₂-CH₂-SO₂-), 2.84 and 2.96 (m, 1H, 1H, -Si-CHCH₃-CH₂-SO₂-), 2.95 (m, 2H, -Si-(CH₂)₂-CH₂-SO₂-) 3.01(m, 2H, -SO₂-CH₂-(CH₂)₈-CH₃).

$^{13}\text{C-NMR}$ (CDCl_3): $\delta = -0.1$ (s, 1C, $-\text{Si-CH}_3$), 13.97 (s, 1C, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 14.39 (s, 1C, $-(\text{CH}_2)_9\text{-CH}_3$), 15.68 (s, 1C, $-\text{Si-CH}_2\text{-CH}_2\text{-CH}_2-$), 16.60 (s, 1C, $-\text{Si-CH}_2\text{-CH}_2-$), 21.98 (s, 1C, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 22.00 (s, 1C, $-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2-$), 22.88 (s, 1C, $-(\text{CH}_2)_6\text{-CH}_2\text{-CH}_3$), 28.83-32.18 (s, 6C, $-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-(CH}_2)_6\text{-CH}_2\text{-CH}_3$), 53.48 (s, 1C, $-\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-SO}_2-$), 54.26 (s, 1C, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 55.09 (s, 2C, $-\text{SO}_2\text{-CH}_2\text{-CH}_2-$).

12SP $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.16$ (s, 3H, $-\text{Si-CH}_3$), 0.72 (t, 2H, $-\text{Si-CH}_2\text{-CH}_2-$), 0.88 (t, 3H, $-(\text{CH}_2)_{11}\text{-CH}_3$), 1.25 (d, 3H, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 1.26 (m, 16H, $-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-(CH}_2)_8\text{-CH}_3$), 1.43 (m, 2H, $-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2-$), 1.71 (m, 1H, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 1.81 (m, 2H, $-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2-$), 1.88 (m, 2H, $-\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-SO}_2-$), 2.84 and 2.96 (m, 1H, 1H, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 2.97 (m, 2H, $-\text{Si-(CH}_2)_2\text{-CH}_2\text{-SO}_2-$) 3.01 (m, 2H, $-\text{SO}_2\text{-CH}_2\text{-(CH}_2)_{10}\text{-CH}_3$).

$^{13}\text{C-NMR}$ (CDCl_3): $\delta = -0.1$ (s, 1C, $-\text{Si-CH}_3$), 14.00 (s, 1C, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 14.46 (s, 1C, $-(\text{CH}_2)_{11}\text{-CH}_3$), 15.71 (s, 1C, $-\text{Si-CH}_2\text{-CH}_2\text{-CH}_2-$), 16.66 (s, 1C, $-\text{Si-CH}_2\text{-CH}_2-$), 22.10 (s, 1C, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 22.17 (s, 1C, $-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2-$), 22.98 (s, 1C, $-(\text{CH}_2)_8\text{-CH}_2\text{-CH}_3$), 28.97-32.26 (s, 8C, $-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-(CH}_2)_8\text{-CH}_2\text{-CH}_3$), 53.59 (s, 1C, $-\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-SO}_2-$), 54.47 (s, 1C, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 55.35 (s, 2C, $-\text{SO}_2\text{-CH}_2\text{-CH}_2-$).

14SP $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.17$ (s, 3H, $-\text{Si-CH}_3$), 0.72 (t, 2H, $-\text{Si-CH}_2\text{-CH}_2-$), 0.88 (t, 3H, $-(\text{CH}_2)_{13}\text{-CH}_3$), 1.25 (d, 3H, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 1.26 (m, 20H, $-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-(CH}_2)_{10}\text{-CH}_3$), 1.43 (m, 2H, $-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2-$), 1.68 (m, 1H, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 1.81 (m, 2H, $-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2-$), 1.91 (m, 2H, $-\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-SO}_2-$), 2.84 and 2.97 (m, 1H, 1H, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 2.92 (m, 2H, $-\text{Si-(CH}_2)_2\text{-CH}_2\text{-SO}_2-$) 3.01 (m, 2H, $-\text{SO}_2\text{-CH}_2\text{-(CH}_2)_{12}\text{-CH}_3$).

$^{13}\text{C-NMR}$ (CDCl_3): $\delta = -0.1$ (s, 1C, $-\text{Si-CH}_3$), 13.67 (s, 1C, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 14.10 (s, 1C, $-(\text{CH}_2)_{13}\text{-CH}_3$), 15.35 (s, 1C, $-\text{Si-CH}_2\text{-CH}_2\text{-CH}_2-$), 16.28 (s, 1C, $-\text{Si-CH}_2\text{-CH}_2-$), 21.58 (s, 1C, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 21.79 (s, 1C, $-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2-$), 22.67 (s, 1C, $-(\text{CH}_2)_{10}\text{-CH}_2\text{-CH}_3$), 28.59-31.89 (s, 10C, $-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-(CH}_2)_{10}\text{-CH}_2\text{-CH}_3$), 53.18 (s, 1C, $-\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-SO}_2-$), 54.05 (s, 1C, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 54.92 (s, 2C, $-\text{SO}_2\text{-CH}_2\text{-CH}_2-$).

16SP $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.16$ (s, 3H, $-\text{Si-CH}_3$), 0.72 (t, 2H, $-\text{Si-CH}_2\text{-CH}_2-$), 0.88 (t, 3H, $-(\text{CH}_2)_{15}\text{-CH}_3$), 1.25 (d, 3H, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 1.26 (m, 24H, $-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-(CH}_2)_{12}\text{-CH}_3$), 1.43 (m, 2H, $-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2-$), 1.71 (m, 1H, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 1.82 (m, 2H, $-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2-$), 1.88 (m, 2H, $-\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-SO}_2-$), 2.85 and 2.97 (m, 1H, 1H, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 2.95 (m, 2H, $-\text{Si-(CH}_2)_2\text{-CH}_2\text{-SO}_2-$) 3.01 (m, 2H, $-\text{SO}_2\text{-CH}_2\text{-(CH}_2)_{14}\text{-CH}_3$).

$^{13}\text{C-NMR}$ (CDCl_3): $\delta = -0.1$ (s, 1C, $-\text{Si-CH}_3$), 13.70 (s, 1C, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 14.30 (s, 1C, $-(\text{CH}_2)_9\text{-CH}_3$), 16.09 (s, 1C, $-\text{Si-CH}_2\text{-CH}_2\text{-CH}_2-$), 17.00 (s, 1C, $-\text{Si-CH}_2\text{-CH}_2-$), 22.50 (s, 1C, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 22.55 (s, 1C, $-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2-$), 23.05 (s, 1C, $-(\text{CH}_2)_6\text{-CH}_2\text{-CH}_3$), 29.19-32.68 (s, 6C, $-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-(CH}_2)_6\text{-CH}_2\text{-CH}_3$), 53.93 (s, 1C, $-\text{Si-CH}_2\text{-CH}_2-$),

$\text{CH}_2\text{-SO}_2-$), 54.85 (s, 1C, $-\text{Si-CHCH}_3\text{-CH}_2\text{-SO}_2-$), 55.72 (s, 2C, $-\text{SO}_2\text{-CH}_2\text{-CH}_2-$).

Results and Discussion

(3-*n*-Alkylthio)propyl-substituted poly(methylsiloxane) (nTPs: *n* = 8, 10, 12, 14, 16) were synthesized by a hydrosilylation reaction using a Speier's Pt catalyst, starting from poly(methylhydrosiloxane) (PMHS) with the corresponding (3-*n*-alkylthio)propenes, where the (3-*n*-alkylthio)propenes were prepared from the allylation of the allyl bromide with corresponding sodium thiolate (Figure 1). In this hydrosilylation reaction, we used 10 mol% excess of (3-*n*-alkylthio)propenes over the Si-H groups in PMHS, which is commonly used for the hydrosilylation of PMHS.^{9,10} FT-IR analysis of nTPs showed that the hydrosilylation reaction was complete, since the absorption band at 2160 cm^{-1} rising from the Si-H group in the starting polymer, PMHS, was not observed in the product.^{11,12} However, $^1\text{H-NMR}$ spectrum of the nTPs showed a very low intensity 4.8 ppm peak from the unsubstituted Si-H group (Figures 2(a) and (b)). The conversions from PMHS to nTPs were calculated by comparing the intensity of the triplet peak at 0.88 ppm of the methyl end group on the side chain and that of the singlet at 4.8 ppm of the Si-H group in the backbone, and they were always higher than 95%. Thus, the conversion from PMHS to nTPs using hydrosilylation is very high, although resolution difference between $^1\text{H-NMR}$ and FT-IR could contribute to difference in the observed conversions.

Polymers were further examined by 2-dimensional heterogeneous NMR spectroscopy to assign all superimposed $^1\text{H-NMR}$ peaks. The 2-dimensional NMR result for 10TP is shown in Figure 3. In general, hydrosilylation of PMHS using platinum catalysts undergo anti-Markovnikov addition of hydrosilane groups to the carbon-carbon double bonds.¹³⁻¹⁵ However, subtle differences in the catalyst and reagents afford some degree of Markovnikov addition.¹⁶ In our case,

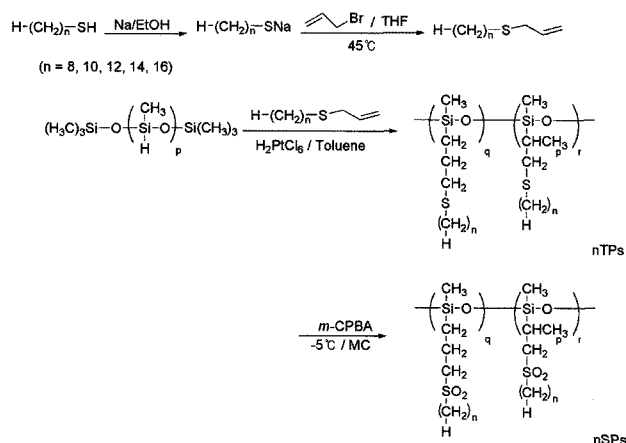


Figure 1. Synthetic route for nTPs and nSPs.

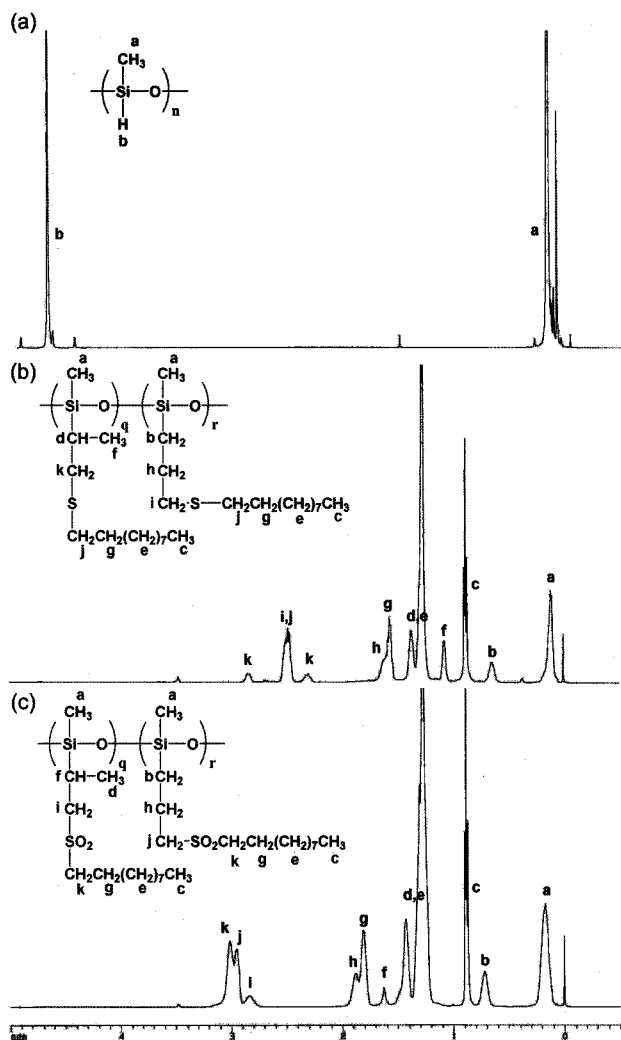


Figure 2. $^1\text{H-NMR}$ of PMHS, 10TP, and 10SP.

the ratio between propyl ($-\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-S-}$) produced from anti-Markovnikov addition and 1-methyl ethyl ($-\text{Si-CH(CH}_3\text{)-CH}_2\text{-S-}$) produced from Markovnikov addition is about 1:1 for all nTPs. This ratio was calculated by comparing $^1\text{H-NMR}$ integration of peaks at 0.65 ppm (b peak in Figure 2(b)) from anti-Markovnikov addition and 1.06 ppm (f peak in Figure 2(b)) from Markovnikov addition. It has been known that some functional groups in allyl reagents can cause side reactions, including Markovnikov addition.¹⁶ For example the hydrosilylation reaction of PMHS with allyl ester or allyl carbamate produces Markovnikov products.^{17,18} The high content of products from Markovnikov's rule in our case is probably due to the existence of the thioether groups in the (3-*n*-alkyl- thio)propene; thioether groups have highly coordinating capability with metallic ions.¹⁹

(3-*n*-Alkylsulfonyl)propyl-substituted poly(methylsiloxane)s (nSPs: $n = 8, 10, 12, 14, 16$) were synthesized by oxidation of the corresponding nTPs using *m*-chloroperoxybenzoic acid (*m*-CPBA) (Figure 1). $^1\text{H-NMR}$ spectra results indicated

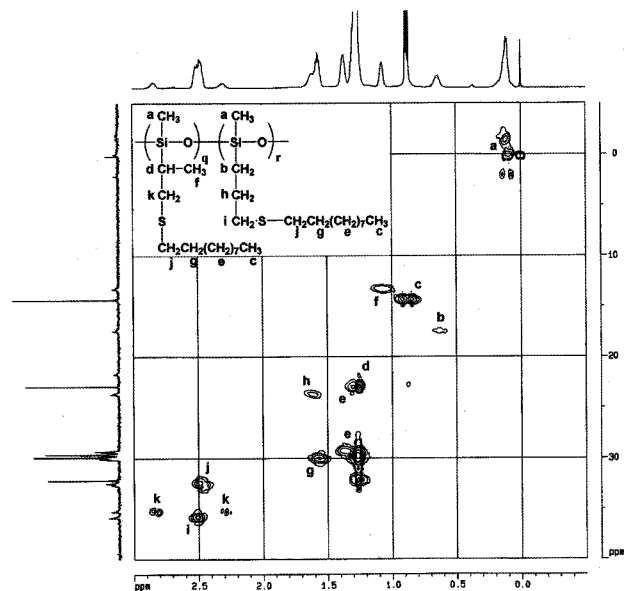
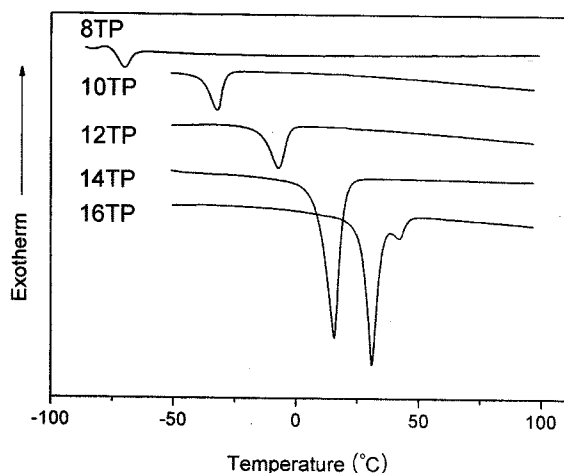
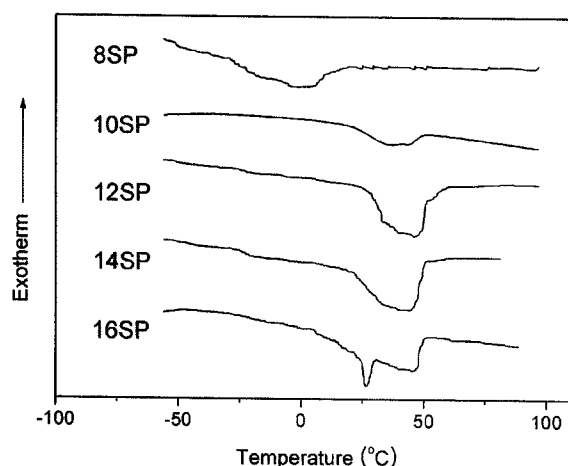


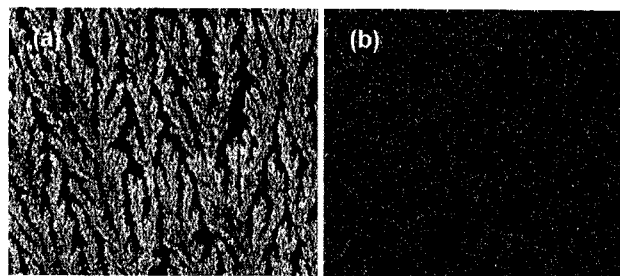
Figure 3. 2-Dimensional heterogeneous NMR of 10TP.

100% conversion from nTPs to nSPs (Figure 2(c)). The polymer analogous reaction from poly(methylhydrosiloxane) to nTPs increased the molecular weight of the polymer. The M_n of nTPs are between 5,200 and 10,300, which are about 2.5 to 4.5 times larger than that of the starting polymer, poly(methylhydrosiloxane). The increase in the molecular weight from the polymer analogous reactions is expected, since (3-*n*-alkylthio)propenes are additionally incorporated into the poly(methylhydrosiloxane) backbone. The increased molecular weights of nTPs were maintained after the oxidation reaction to nSPs: the M_n of nSPs are between 5,200 and 9,900. Since the molecular weights of these polymers were obtained by gel permeation chromatography using polystyrene standards, the direct comparison of these values is not possible. The variations in molecular weight data can be attributed to a variety of factors that affect the actual size and shape of a polymer molecule in solution, including changes in side group-solvent interactions and polymer conformations that result from the incorporation of the side alkyl groups and the sulfur groups.²⁰ Regardless, the molecular weight results show that the polymer analogous reaction did not cleave the polymer backbone.

Figures 4 and 5 show DSC heating thermograms for the polymers obtained during the second heating cycle at a rate of 10 °C/min; relatively sharp and broad endotherms are observed from nTPs and nSPs, respectively. The transition temperatures and enthalpy changes (ΔH) of the polymers are summarized in Table I. For the enthalpy changes of multiple melting peaks, we just integrated the superimposed peaks without any deconvolution process. No melting or glass transition from the siloxane backbone, which occur at temperatures lower than -100 °C, were observed. Therefore, the endotherms in the DSC traces originated from ordered


Figure 4. DSC second heating curves of nTPs.

Figure 5. DSC second heating curves of nSPs.

structures in the side chains. Similarly, poly(methylalkylsiloxane)s also showed endotherms associated with the melt-


Figure 6. (a) POM texture of 16TP and (b) POM texture of 16SP.

ing of the side chain crystalline phases.⁶ The endotherms of nTPs and nSPs were found to be originated from side chain crystalline and liquid crystalline phases, respectively, from polarizing optical microscopy and X-ray studies discussed below. Both endothermic temperatures and ΔH increase with increasing side chain length. For a given side chain length, the endothermic temperatures of nSPs are higher than those of nTPs. This was mainly attributed to the strong dipole-dipole interaction between sulfone groups in the side chain.²¹ The existence of a strong dipolar moment for the sulfonyl group ($-\text{SO}_2-$) is well documented.²²

The ordered structures of the polymers were investigated using polarizing optical microscopy (POM). nTPs ($n = 8, 10, 12,$ and 14) were in an isotropic melt state at room temperature because the endothermic temperatures of these polymers are lower than room temperature; only dark phases were observed from POM. However, 16TP and nSPs ($n = 10, 12, 14,$ and 16) showed birefringent images. When 16TP was cooled from the isotropic melt state, very thin birefringent rods started to appear at around 45°C . Within a few minutes, these rods become more birefringent and thicker, finally becoming the leap-shaped texture shown in Figure 6(a). Thus, the formation of an ordered phase of 16TP involves the nucleation and growth process commonly found from crystalline polymers. All nSPs showed the same fine granu-

Table I. GPC, DSC, and Polarizing Optical Microscopy Results of the Polymers

Polymer	M_w	M_n	M_w/M_n	First Cooling Endotherm, $^\circ\text{C}$ (ΔH , J/g)	Second Heating Exotherm, $^\circ\text{C}$ (ΔH , J/g)	Texture ^a
8TP	10,600	5,200	2.02	-81.3 (6.4)	-70.0 (5.3)	
10TP	34,600	10,300	3.36	-37.8 (14.2)	-32.3 (15.4)	
12TP	12,700	5,900	2.17	-12.9 (13.7)	-7.3 (14.5)	
14TP	14,900	6,900	2.17	6.50 (53.8)	15.6 (57.8)	
16TP	17,900	8,200	2.19	23.0 (72.8)	32.5 (71.5)	Spherulite
8SP	20,600	5,200	3.98	-14.9 (9.2)	-4.8 (11.2)	
10SP	18,100	9,900	1.84	38.0 (15.8)	36.0 (19.4)	Grainy
12SP	23,000	8,000	2.89	31.6 (26.0)	41.3 (25.4)	Grainy
14SP	10,600	5,600	1.88	43.5 (43.4)	51.6 (50.8)	Grainy
16SP	14,900	6,000	2.47	56.3 (57.8)	66.4 (63.8)	Grainy

^aObtained from heating at $10^\circ\text{C}/\text{min}$ using POM.

lated texture shown in Figure 6(b) at around their endothermic temperatures when they were cooled from the isotropic melt state, while the nucleation and growth procedure found from 16TP was not observed. Viscous polymer melts can prevent the formation of normal liquid crystalline textures.²¹ This is especially true for smectic liquid crystalline polymers and a granulated texture of birefringent domains is observed in many cases. Therefore, it is very probable that nSPs have a liquid crystalline phase.

X-ray studies also confirmed the crystallinity of 16TP and the liquid crystallinity of nSPs. Figure 7 shows the X-ray powder patterns at room temperature and elevated temperature for 16TP. The small-angle and wide-angle d -spacings of each polymer are listed in Table II. The d -spacing value of 16TP in the wide-angle region corresponding to the distance between alkyl side chains, 4.16 Å, is near the typical hexagonal d -spacing value of 4.10–4.19 Å for other comb-like polymers with long alkyl side chains.^{5,23,24} Therefore, POM images and wide-angle x-ray powder diffraction indicate that 16TP has a typical hexagonal packing of the long alkyl side chains. Above its melting transition, the sharp wide-angle reflection changes to an amorphous halo (Figure 7). At 40 °C, several peaks from the ordered structures left while their intensity is very small. Since the melting transi-

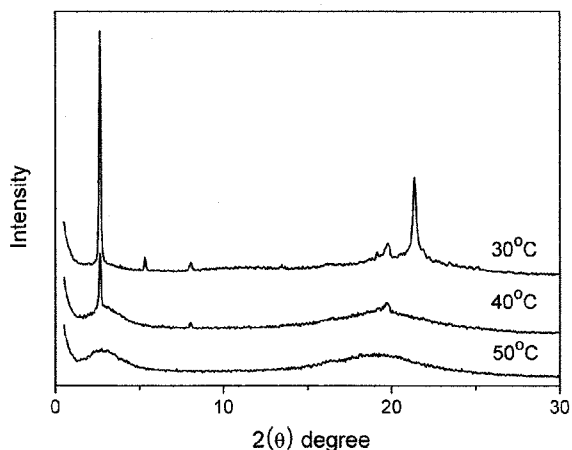


Figure 7. Powder XRD patterns at room temperature and elevated temperatures for 16TP.

Table II. The d -Spacings Determined from the Most Intensive Peak in the Wide-Angle Region and from the First Diffraction in the Small-Angle Region, and the Side Chain Length (L_{cal})

Polymer	Wide-angle (Å)	Small-angle (Å)	$2 \times L_{cal}$ (Å)
10SP	4.43	36.51	39.46
12SP	4.34	41.28	44.46
14SP	4.32	42.48	49.46
16SP	4.22	37.08	54.46
16TP	4.16	33.30	54.62

tion remains until around 50 °C, these small peaks should be due to the small portion of ordered structures remaining in the polymer. A series of sharp peaks at $d = 33.30$, 16.65, and 11.00 Å, corresponding to 001, 002, and 003 indices of the periodic layer, were observed at 30 °C, implying that 16TP has a highly-ordered layer structure. Therefore, the ordered structure of 16TP is almost identical to other comb-like polymers with long alkyl side chains that show side chain crystallization.

On the other hand, the d -spacing value of nSPs ($n = 10, 12, 14,$ and 16) in the wide-angle region (Figure 8) is unusually large, ranging from 4.22 to 4.43 Å. In general, when the carbon numbers of alkyl side chain is more than 12, one or more sharp wide-angle diffraction of less than 4.2 Å occurs in comb-like vinyl polymers,^{24–26} rigid-rod polymers,^{27,28} and amphiphilic polymers with long alkyl side chains.^{29,30} This large d -spacing of 16SP in the wide-angle region, 4.22 Å,

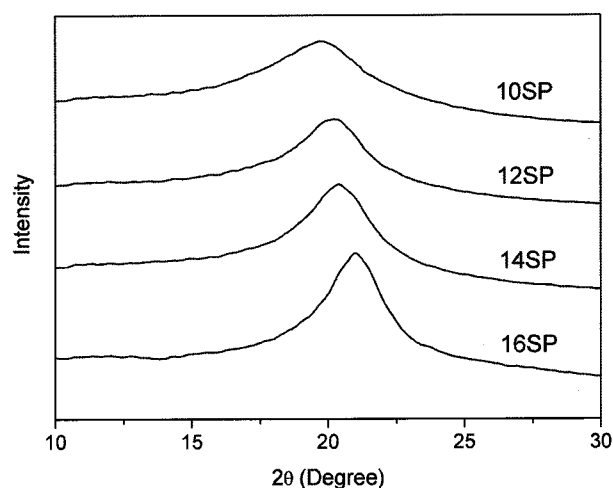


Figure 8. Powder XRD patterns at room temperature for nSPs: wide angle region.

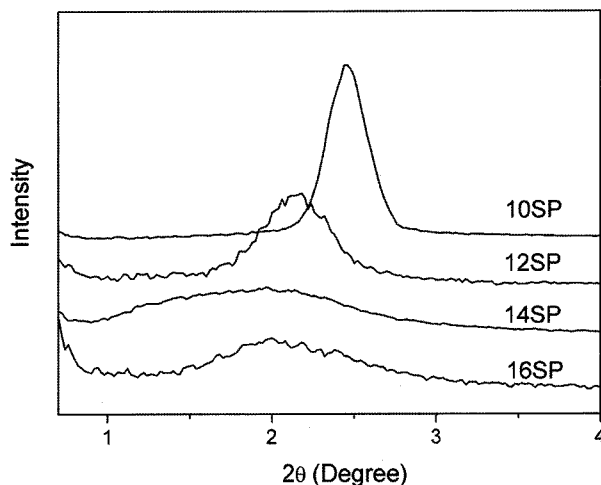


Figure 9. Powder XRD patterns at room temperature for nSPs: small angle region.

indicates that paraffinic side chain crystallization does not occur. Instead, a less ordered structure, such as liquid crystal (smectic A or smectic B) or conditic crystal, develops through strong dipole-dipole interactions between sulfone groups.³¹

In the small-angle region of nSPs (Figure 9), a series of diffraction peaks were observed. These peaks indicate that our polymers have ordered layers. The d -spacings from the first reflection in the small-angle region are listed in Table II. The small-angle d -spacings of the polymers were larger than the calculated side chain length (L_{cal}) but smaller than $2 \times L_{cal}$; the calculated side chain length, L_{cal} , was estimated based on the assumption that the side chains are fully extended in the trans conformations. This result indicates that the polymers have double-layer structures, with tilted or interdigitated side groups. Further studies using 2-dimensional X-ray measurements of oriented fibers are needed to verify whether these polymers have tilted or interdigitated structures.³² Unfortunately, the preparation of oriented fibers from these polymers was not possible, probably because of the low molecular weights. We could not increase the molecular weight of the polymer because the molecular weight of the starting polymer, PHMS, is low. High molecular weight of PHMS is difficult to prepare due to the sensitivity of Si-H bond.³³

In conclusion, nSPs (polymers with sulfone linking groups) show mesomorphic behavior and a double layer structure, while 16TP with thioether linking groups has typical side chain crystalline phases. The side chain crystalline behavior of 16TPs occur because the increased mobility of the siloxane main chain does not dramatically inhibit crystallization.^{34,35} Increasing the flexibility of the main chain increases the probability of formation of an ordered structure.³⁶ The mesophase formation of nSPs arises from phase separation caused by the incompatibility between polar and hydrophilic sulfone linking group and hydrophobic backbone and side groups and/or the strong dipole-dipole interactions between the sulfone groups, which create the stiff section or the mesogenic unit in the polymer.

Conclusions

Poly(methylsiloxane)s with alkylthio or alkylsulfonyl side groups were successfully synthesized using polymer analogous reactions. Poly(methylsiloxane)s with alkylthio side groups show side chain crystalline properties, whereas poly(methylsiloxane)s with alkylsulfonyl side groups showed liquid crystalline phases. Thus, the inter- or intramolecular interactions modify and reinforce the organized phases. Poly(methylsiloxane)s with only one less polar alkylthioether group do not have liquid crystallinity, possibly because the polymer structure is not symmetric or they cannot produce phase separation to induce the biphilicity. The polar alkylsulfonyl side groups attached to the siloxane backbones can generate dipolar interactions between the side chains in parallel, and

promote their arrangement in layered mesomorphic phases. Phase separation caused by the strong incompatibility between the polar and hydrophilic sulfone linking groups, and hydrophobic backbone and side groups, induces the liquid crystalline structures. Therefore, in addition to main chain flexibility, phase separation, the dipole-dipole interactions between the polar sulfone groups can generate and control the ordered structures of the polymeric materials in a rather unique manner.

Acknowledgements. Financial supports of this work by Korea Science and Engineering Foundation through the Basic Research Program (grant No. R01-2006-000-10749-0) and Seoul Research Business & Development Program (grant No. 10538) is gratefully acknowledged. Experiments at PAL were supported in part by MOST and POSCO.

References

- (1) T.-S. Chung, *Thermotropic Liquid Crystal Polymers: Thin-film Polymerization, Characterization, Blends, and Applications*, Technomic Publishing Company, 2001, Chap. 1.
- (2) J.-I. Jin and C.-S. Kang, *Prog. Polym. Sci.*, **22**, 937 (1997).
- (3) J. S. Derek, in *Liquid Crystal Polymers: From Structures to Applications*, A. A. Collyer, Ed., Elsevier Applied Science, London and New York, 1992, Chap. 7-8.
- (4) Y. K. Godovsky, I. I. Mamaeva, N. N. Makarova, V. S. Papkov, and N. N. Kuzmin, *Makromol. Chem. Rapid Commun.*, **6**, 797 (1985).
- (5) G. J. J. Out, A. A. Turetskii, M. Möller, and D. Oelfin, *Macromolecules*, **27**, 3310 (1994).
- (6) P. B. Rim, H. A. A. Rasoul, S. M. Hurley, E. B. Orler, and K. M. Scholsky, *Macromolecules*, **20**, 208 (1987).
- (7) T. Zhang, M. H. Litt, and C. E. Rogers, *J. Polym. Sci.; Part A: Polym. Chem.*, **32**, 2291 (1994).
- (8) J.-C. Lee, M. H. Litt, and C. E. Rogers, *Macromolecules*, **31**, 2440 (1998).
- (9) M. M. Doeff and E. Lindner, *Macromolecules*, **22**, 2951 (1989).
- (10) Y. Kawakami, Y. Li, Y. Liu, M. Seino, C. Pakjamsai, M. Oishi, Y. H. Cho, and I. Imae, *Macromol. Res.*, **12**, 156 (2004).
- (11) A. A. Thorpe, T. G. Nevell, and J. Tsibouklis, *Appl. Surf. Sci.*, **137**, 1 (1999).
- (12) S. H. Lee, W. S. Jahng, K. H. Park, N. J. Kim, W.-J. Joo, and D. H. Choi, *Macromol. Res.*, **11**, 431 (2003).
- (13) B. Boutevin, F. Guida-Pietrasanta, and A. Ratsimihety, *J. Polym. Sci.; Part A: Polym. Chem.*, **38**, 3722 (2000).
- (14) Y. Furukawa and M. Kotera, *J. Polym. Sci.; Part A: Polym. Chem.*, **40**, 3120 (2002).
- (15) S. Y. Pyun and W. G. Kim, *Macromol. Res.*, **11**, 202 (2003).
- (16) M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry*, A Wiley-Interscience Publication, 1999, pp 404-412.
- (17) C. B. McArdle, *Side Chain Liquid Crystal Polymers*, Blackie, Chapman and Hall, New York, 1989, pp 110-114.
- (18) J. M. Yu, D. Teyssie, and S. Boileau, *J. Polym. Sci.; Part A: Polym. Chem.*, **31**, 2373 (1993).

- (19) V. Srinivasan, E. I. Stiefel, A. Elsberry, and R. A. Walton, *J. Am. Chem. Soc.*, **101**, 2611 (1979).
- (20) L. H. Sperling, *Introduction to Physical Polymer Science*, A Wiley-Interscience Publication, 1992, Chapter 3.
- (21) J.-C. Lee, S.-H. Han, S.-H. Cha, S. Y. Park, and B. L. Farmer, *Polymer*, **44**, 7413 (2003).
- (22) A. C. Fantoni and G. Corbelli, *J. Mol. Spec.*, **164**, 319 (1994).
- (23) N. A. Plate and V. P. Shibaev, *J. Polymer. Sci.; Macromol. Rev.*, **8**, 117 (1974).
- (24) F. Andruzzi, D. Lupinacci, and P. L. Magagnini, *Macromolecules*, **13**, 15 (1980).
- (25) K. Yokota, T. Kougo, and T. Hirabayashi, *Polym. J.*, **15**, 891 (1983).
- (26) Y. Yuki, H. Kunisada, and Y. Miyake, *Polym. J.*, **23**, 939 (1991).
- (27) M. Ballauff and G. F. Schmit, *Mol. Cryst. Liq. Cryst.*, **147**, 163 (1987).
- (28) J. M. Rodriguez-Parada, R. Duran, and G. Wegner, *Macromolecules*, **22**, 2507 (1989).
- (29) T.-M. Chen, Y.-F. Wang, M. Kitamura, T. Nakawa, and I. Sakurai, *J. Polym. Sci.; Polym. Chem.*, **34**, 1155 (1996).
- (30) T. Takahashi, T. Kimura, and K. Sakurai, *Polymer*, **40**, 5939 (1999).
- (31) B. Wunderlich, *Thermochim. Acta*, **37**, 340 (1999).
- (32) S.-Y. Park, T. Zhang, L. V. Interrante, and B. L. Farmer, *Polymer*, **43**, 5169 (2002).
- (33) S. Maisonnier, J.-C. Favier, M. Masure, and P. Hémerly, *Polym. Int.*, **48**, 159 (1999).
- (34) P. B. Rim, *Polym. Commun.*, **27**, 199 (1986).
- (35) E. F. Jordon, D. W. Feldeisen, and A. N. Wrigley, *J. Polym. Sci.; Polym. Chem.*, **9**, 1835 (1971).
- (36) V. V. Volkov, N. A. Platé, A. Takahara, T. Kajiyama, N. Amaya, and Y. Murata, *Polymer*, **33**, 1316 (1992).